Process for preparing CaF$_2$ lens blanks especially for
193 nm and 157 nm lithography with minimized defects

The invention relates to a process for preparing CaF$_2$ lens
blanks for 193 nm and 157 nm lithography and their use in
preparing electronic means.

Homogeneity residuals of the refractive index have a strong
influence on the performance of lithography tools for both
193 and 157 nm application wavelengths. By systematic in-
vestigations of various defects in the real structure of
CaF$_2$ crystals, the origin of homogeneity residuals can be
shown. Based on a quantitative analysis we define limiting
values for the individual defects which can be either tol-
erated or controlled by optimized process steps, e.g. an-
nealing. These correlations were carried out for all three
relevant main crystal lattice orientations of CaF$_2$ blanks.
In conclusion we achieved a strong improvement of the
critical parameters of both refractive index homogeneity
and striae for large size lens blanks up to 270mm diameter.

The trend towards ever smaller structures in semiconductor
devices is still driven by Moores Law. A major part in the
production process for semiconductor devices is optical li-
thography. The optics used in these lithography tools re-
quire materials of exceptional high quality. Due to the ap-
plication wavelength of 193nm or in the future 157nm CaF$_2$
single crystalline lenses are a major part in the optics of
this systems. Among other parameters the refractive index
homogeneity has a strong influence on the image quality.

G. Grabosch, K. Knapp, E. Moersen: "Status of the CaF$_2$ Pro-
gram at Schott Lithotec", 2nd International Sematech 157nm
Technical Data Review Meeting, May 2002; G. Grabosch, K.

Knapp, L. Parthier, Th. Westerhoff, E. Moersen: "Calcium Fluoride Quality Improvements Support Availability of First F_2 Lithography Tools", 3rd International Sematech 157nm Technical Data Review Meeting, Sep. 2002; and J. Hahn, G. Grabosch, L. Parthier, K. Knapp: "Quality Status for 157nm Exposure Tools", International Sematech & Selete 4th International Symposium on 157nm Lithography, Aug. 2003 describe that during the production of CaF_2 single crystals several process steps will influence the optical property of the material. In order to further optimize the various defects occurring due to real crystal structure, their influence on optical homogeneity and a method of controlling them during processing were now investigated by the present inventors.

The parameters in homogeneity of the refractive index and stress-induced birefringence (SDB) must also be very low, even for lenses having large diameters. Thereby these parameters should preferably show an residual inhomogeneity (after subtraction of 36 Zernike coefficients or terms) of lower than 0.02 ppm ($2x10^{-8}$) and the SDB-(RMS) should preferably be less than 0.2 nm/cm in the (111) direction, in the (100) direction it should be less than 0.4 nm/cm. This can be obtained by an optimized annealing in a separate temperature furnace which preferably is optimally constructed, as it is described e.g. in DE 10 2004 008 754 A1, DE 10 2004 008 753 A1, DE 10 2004 008 752 A1 and DE 100 10 485 A1.

These quality parameters are now not anymore determined by global, i. e. wide-ranging defects in crystal structures and characteristics but are rather determined by local inhomogeneities. These local inhomogeneities are based on different local defects in the theoretically completely pe-

.riodical crystal structure. In the present invention the influence of each single defect has been investigated on local effects, e.g. as optical inhomogeneity before and after annealing. The influence of annealing has been investigated for each main orientation (111, 100, 110) on CaF$_2$ blanks. The invention now enables to determine limits for each structural defect and each main orientation before the annealing, thus making it possible to achieve aimed parameters by an adopted, e.g. high temperature, annealing.

The most common crystal defects affecting the refractive index homogeneity in CaF$_2$ are slip planes and small angle grain boundaries and other local real structure defects.

The main method of plastic deformation of crystals is glide. During gliding one part of the crystal is displaced relative to another. Glide occurs over definite crystallographic planes along definite directions. The planes along which the crystal layers move are the slip planes and the direction of the displacement is the slip direction. On a microscopic scale the glide process can be explained with the movement of dislocations through the crystal. A set of all crystallographically equivalent slip planes and directions forms a glide system. For CaF$_2$ the principle glide system is {100}/<110>. Further glide systems are {110} / <110> and at higher temperatures {111} / <110> (see L. A. Shuvalov ed.: "Modern Crystallography IV" Springer Series in Solid State Sciences 37, pp. 77).

Small angle grain boundaries are two dimensional lattice defects comprised of a number of step and / or screw dislocations. They are confined to small volumes. Depending on the misorientation angle, the inclination of the grain

boundary and the translational displacement between neigh-
boring sub grains, two types of sub grain boundaries can be
distinguished: tilt and twist boundaries. One refers to
small angle grain boundaries in case the difference in ori-
entation is small, i.e. in the range of minutes up to a few
degrees. Small angle grain boundaries can be formed e. g.
during crystal growth caused by thermal fluctuations at the
solid liquid interface and or impurities at the interface.
Normally small angle grain boundaries are accompanied by a
short range stress field.

In some cases small angle grain boundaries rearrange and
form more extended structures. These structures are not
aligned to a specific crystallographic direction and occur
as a local distortion in the homogeneity interferograms.
These distortions have also a detrimental effect on the op-
tical image quality.

Each optical medium shows dispersion, i.e. its diffraction
is dependent upon the wave length. Accordingly, any real
picture imaged by a lens system is a summary of overlayed
monochromatic images. Only narrow light sources like a la-
ser are able to limit these types of aberration. Besides
this, any impairment of the geometrical form of an optical
lens creates aberration leading to a decrease in resolu-
tion.

It is well known to describe waves and wave fronts of an
optical system mathematically by series expansion. For op-
tical application the Zernike polynome is often used, which
describes a wave front as a summary of terms.

$$W(x,y) = \sum_{i=1}^{n} C_i Z_i(x,y)$$

·In this polynome each Zernike coefficient can be assigned
to a discrete type of aberration. For example, coefficient
C_1 describes the tilt in the x-axes, C_2 the tilt in y-axes,
C_3 the astigmatism in ± 45°, C_4 describes the defocus, C_5
the astigmatism in 0° and 90° and so on.

The wave fronts of such optical systems can be detected by
several ways, e.g. by means of a CCD camera.

Fig. 1 shows the influence of Zernike terms subtracted on
PV (Peak to Valley, which is the maximal difference between
the highest and lowest value measured within a blank.) and
RMS value (root mean square).

In applicants ongoing effort for quality improvement the
influence of the annealing process on the homogeneity in
(100), (110) and (111) oriented CaF_2 lens blanks has been
investigated. Therefore homogeneity wave fronts were taken
under the same conditions before and after annealing. The
interferometer used is a ZEISS D100 Fizeau type interfer-
ometer, the spatial resolution was 0.2 μm. Before analyzing
the wave fronts for crystal defects the first 36 Zernike
terms were subtracted. In this residual wave front crystal
defects can be detected and analyzed more easily. A sub-
traction of further Zernike terms did not improve the re-
sults due to an asymptotic effect on PV and RMS as shown in
Figure 1.

Fig. 2 shows an example of performed fitting of a defect
structure cross section before annealing (thin line), and
after annealing (bold line).

The analysis has been performed as follows:

Before and after annealing the strongest defect structures
in the wave front was analyzed. Then for the individual de-
fect structures a Gaussian fit of the cross sections was
performed. It is also possible to use other types of best
fit functions known in the art, as for example a Lorentz
fit. The fit provides values for amplitude (height), corre-
sponding to delta n (refractive index) and half width (in
mm). The observed change in amplitude and half width due to
annealing of corresponding defect structures are calculated
relative to the starting value.

Fig. 3 shows a cross section scan in homogeneity wave front
before (Fig. 3a) and after annealing (Fig. 3b) of a crys-
tal.

For a better illustration of the applied procedure in the
following the analysis considering as example a blank with
untypical high defect level (Figure 3 a, b) will be dis-
cussed. Homogeneity wave fronts after subtraction of the
first 36 Zernike terms before and after annealing is com-
pared. After annealing an improvement of the total residual
structure can clearly be seen. Whereas before annealing the
homogeneity is dominated or disturbed by long range struc-
tures, after annealing homogeneity is more affected by the
short range defect structures. The relative improvement of
RMS-Residual is about 30%. While the maximum amplitude of a
single local structure defect could be reduced to 60% of
the starting value the corresponding maximum half width
could be minimized down to 30%.

Each defect structure observed is categorized for type and
blank orientation For the values found typical for the de-

·fect behavior the mean value was calculated. The results
obtained are discussed below.

The annealing process has only a very small influence on
small angle grain boundaries in {111} oriented lens blanks.
The reduction of the amplitude was in the range of about
20%, the width was nearly constant. For other orientations
a similar behavior can be achieved.

In a modified form small angle grain boundaries generate
more extended defect structures. In spite of the "normal"
small angle grain boundary we find a clear orientation de-
pendence for the annealing performance. While we obtained a
20 % reduction for the amplitude and about 30% for the half
width for {100} and {110} orientation, whereas the values
for {111} a mostly unchanged.

During the annealing process slip planes become activated
and relax along glide systems. For CaF_2 this is in general
the {100} / <110> glide system. In case small angle grain
boundaries are present they can hamper the relaxation of
the slip planes.

The annealing results show a strong improvement for all
blank orientations. Especially for the {111} orientation
the slip planes can completely disappear. That means slip
planes are not dominating the residual of the refractive
index homogeneity. For the other orientations the amplitude
can be reduced by a factor up to 5.

From the results discussed above applicants have found that
it is now for the first time possible to define critical
maximum values for the different real structure phenomena

·before annealing for each orientation. Under these condi-
tions the annealed lens blanks reach the required quality
for the residual homogeneity.

The invention has therefore for its aim to provide a method
for preparing optical elements especially optical elements
made of crystalline material wherein it is possible to
classify defects in a crystal structure e.g. as slip
planes, small angle grain boundaries, linear structures and
others, as well as mixed structural defects. According to
the invention, an image of a homogeneity (e.g. as shown in
Fig 3) is established (preferably with a CCD-Camera) a sin-
gle structure (defect) is analyzed by measuring homogeneity
in said image and determining the RMS-value (36 Zernike co-
efficients subtracted) for said structure or defect.
Thereby, a line scan is obtained from the structure and the
local defect is identified as a peak. This peak is defined
by a Gaussian fit with the parameters height of the peak
(amplitude) and half-width. Both are found to be absolute
values for the blank as shown in Fig. 2. By integrating the
length of said defect in said homogeneity image, the amount
of the defect can be calculated from the overall value of
the blank. Thereby, the influence of each single defect on
the overall value becomes determinable. The above analysis
is done before and after the annealing of the blank. On the
basis of this analysis, an evaluation of the influence of
each defect structure and defect type in each single blank
on each critical parameter becomes possible. It was found
that a blank having a residual homogeneity (rms) below
2.0×10^{-8} can be obtained if a single local defect, when
analyzed by a Gaussian fit of its cross section, as de-
scribed herein, does not exceed a peak amplitude of maximal

·dn = 5.0×10^{-8} and a half-width below 2mm in its lateral dimension .

According to the invention, it is now possible to effectively determine these blanks for which a annealing is possible and limiting values can be defined.

In the following we present achieved improvements for the most difficult {100} oriented lens blanks.

Through a better approach for describing the blank quality as described above it is now possible to improve the material quality of our CaF_2 lens blank material. The following Table 1 shows the average and standard deviation values achieved for (100) oriented lens blanks for two main quality parameters. The introduction of the advanced conditions lead to a 31% decrease of the stress birefringence RMS value. For the refractive index homogeneity a similar large quality enhancement of about 26% could be realized. Especially the reduction of the short range refractive index homogeneity is of considerably importance since this parameter causes flare in the imaging.

The reproducibility as represented by the standard deviation in line 2 is essential for the production process. For both parameters we achieve a significant progress. For stress birefringence the new conditions lead to reduction of the scattering of the values by a factor of 2. The advancement for homogeneity is even larger. The reduction is of a factor of approx 5. The quality level of these (100) oriented lens blanks meets the currently known requirements for the application in projection optics for both 193nm and 157nm wavelength.

The following Table 1 shows the achieved quality improvement for stress birefringence and short range refractive index homogeneity for (100) oriented CaF_2-crystals:

New conditions		Old conditions	
SBR(rms) average [nm/cm]	Short range refractive index homogeneity, average	SBR(rms) average [nm/cm]	Short range refractive index homogeneity average set =1
0,37	0,74	0,54	1
±0,08	±0,09	±0,16	±0,44

Table 1

Fig. 4 shows the short range refractive index homogeneity for (100) oriented CaF_2 lens blank before (Fig. 4a) and after improvement (Fig. 4b).

Figures 4a and 4b illustrate the reduction of local defect structures as reflected by the short range refractive index homogeneity for champion lens blanks. Figure 4a clearly shows the residual of defect structures after annealing. The remaining structures are mainly slip planes but also small angle grain boundaries in different modifications are visible. Through the measures applied the remaining crystal defects could be reduced to a very low level. Figure 4b shows that the primary slip plane system {100} / <110> has disappeared and only a few traces indicate the secondary system running along {111} / <110>. No other defect structures can be observed. With the present invention lens blanks especially in the 100 blanks having a homogeneity of $2x10^{-8}$ can selectively be obtained. Accordingly, optical

·elements and lens systems, especially for lithography can be achieved with the present invention having superior imaging behavior and a homogeneity in its 100 crystal elements of at least 2×10^{-8} or better. The same can be obtained with 111 blanks.

The invention has therefore also for its aim to prepare lenses, prisms, light conducting rods or optical windows for DUV photolithography, steppers, excimer lasers, computer chips and integrated circuits as well as electronic equipment containing said computer chips and said integrated circuits by means of optical elements obtained by the present classification or selection method.

The influence of various crystal defects on the optical material quality of CaF_2 is determined. With the process of the invention including further improvement of the annealing process applied to critical (100) oriented CaF_2 lens blanks the amount of defect structures can be reduced significantly.

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